

**VERIFICATION OF TRANSLATION**

**U.S. Patent Application Serial No. 10/522,046**

**(based on PCT/JP2003/009227)**

**International Filing Date: 22 July 2003**

**Title of the Invention: GLASS FOR LASER PROCESSING**

I, Yumiko MAKI, whose full post office address is IKEUCHI ·  
SATO & PARTNER PATENT ATTORNEYS, OAP TOWER 26F, 8-30,  
Tenmabashi 1-chome, Kita-ku, Osaka-shi, Osaka 530-6026, JAPAN

am the translator of the document attached and I state that the following  
is a true translation to the best of my knowledge and belief of Japanese  
Patent Application No. 2002-214983 (Date of Application: 24 July 2002).

At Osaka, Japan

Dated this 16/ 1/ 2008 (Day/Month/Year)

Signature of translator:

Yumiko Makii

Yumiko MAKI

PATENT OFFICE  
JAPANESE GOVERNMENT

This is to certify that the annexed is a true copy of the following  
application as filed with this Office.

Date of Application: July 24, 2002

Application Number: Patent Application No. JP 2002-214983

Applicant(s): NIPPON SHEET GLASS COMPANY, LIMITED

[Document Name] Patent Application  
[Case Number] 02P258  
[Destination] Commissioner of the Japan Patent Office  
[Inventor]  
[Address] c/o NIPPON SHEET GLASS COMPANY, LIMITED,  
7-28, Kitahama 4-chome, Chuo-ku, Osaka-shi, Osaka  
[Name] Hirotaka KOYO  
[Inventor]  
[Address] c/o NIPPON SHEET GLASS COMPANY, LIMITED,  
7-28, Kitahama 4-chome, Chuo-ku, Osaka-shi, Osaka  
[Name] Keiji TSUNETOMO  
[Patent Applicant]  
[Identification Number] 000004008  
[Name] NIPPON SHEET GLASS COMPANY, LIMITED  
[Attorney]  
[Identification Number] 100069084  
[Patent Attorney]  
[Name] Seiichi ONO  
[Official Fee]  
[Advance Payment Note Number] 012298  
[Amount of Payment] 21,000 yen  
[List of File Documents]  
[Name of Document] Specification 1  
[Name of Document] Drawing 1  
[Name of Document] Abstract 1  
[General Power of Attorney's Number] 9706787  
[Proof] Required

[Document Name] SPECIFICATION

[TITLE OF THE INVENTION] GLASS FOR LASER PROCESSING

[CLAIMS]

[Claim 1]

A glass for laser processing that can be laser-processed by causing ablation or evaporation by laser beam energy absorbed therein, wherein the glass for laser processing has a composition that satisfies the following conditions:

$60 \leq \text{SiO}_2 + \text{B}_2\text{O} \leq 79 \text{ mol\%}$ ;

$5 \leq \text{Al}_2\text{O}_3 + \text{TiO}_2 \leq 20 \text{ mol\%}$ ; and

$5 \leq \text{Li}_2\text{O} + \text{Na}_2\text{O} + \text{K}_2\text{O} + \text{Rb}_2\text{O} + \text{Cs}_2\text{O} + \text{MgO} + \text{CaO} + \text{SrO} + \text{BaO} \leq 20 \text{ mol\%}$ ,

where  $5 \leq \text{TiO}_2 \leq 20 \text{ mol\%}$ .

[Claim 2]

The glass for laser processing according to claim 1, wherein the composition satisfies the following condition:

$(\text{Al}_2\text{O}_3 + \text{TiO}_2) / (\text{Li}_2\text{O} + \text{Na}_2\text{O} + \text{K}_2\text{O} + \text{Rb}_2\text{O} + \text{Cs}_2\text{O} + \text{MgO} + \text{CaO} + \text{SrO} + \text{BaO}) \leq 0.9$ .

[Claim 3]

The glass for laser processing according to claim 1 or 2, wherein the composition satisfies the following conditions:

$70 \leq \text{SiO}_2 + \text{B}_2\text{O} \leq 79 \text{ mol\%}$ ;

$10 \leq \text{TiO}_2 \leq 15 \text{ mol\%}$ ; and

$10 \leq \text{Na}_2\text{O} \leq 15 \text{ mol\%}$ .

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[Technical field to which the invention pertains]

The present invention relates to a glass laser processing through laser beam irradiation and, in particular, relates to a glass composition that is suitable for laser processing.

[0002]

[Prior Art]

Recently, the technique of processing materials using laser beam energy has been developing gradually to cover the field of micro-processing.

In the processing technique using a mask pattern, the processable length has been extended to the range of nanometers that are further shorter than micrometers due to the progress of the

patterning technique and the shortening of a laser wavelength.

On the other hand, direct processing using a laser also has been practiced in the range of micrometers in the case of processing metal and organic matters such as polyimide as a result of the progress in shortening of the wavelength and pulse width of laser beams.

[0003]

Furthermore, processing such as perforating using a laser is shifting to ablation processing from thermal processing. Ablation is a phenomenon that the state of a material of an irradiation part shifts from melting to evaporation in a short period of time through irradiation of laser beams whose pulse width is very narrow. The level of thermal influence on the periphery of the beam irradiation part varies with an increase or a decrease in pulse width. In the case of processing using an ultrashort pulse laser that completes beam irradiation before thermal diffusion occurs, it is possible to make precise minute holes, with hardly any heat-affected layer being generated.

[0004]

However, many of the lasers that are used for actual processing employ pulse widths of at least the nanosecond order, which makes it impossible to avoid the thermal influence. Hence, a photochemical reaction that is caused by ultraviolet rays is employed. Short-wavelength beams of a laser such as, for instance, an excimer laser have great energy per photon and therefore can cut a chemical bond that forms a molecular skeleton.

[0005]

As described above, the selection of, for instance, the pulse width and wavelength of a laser beam to be used for irradiation conventionally has made it possible to carry out micro-processing. The study, however, has not progressed so much from the viewpoint of improvement of materials to be irradiated with a laser. Processing of glass that is a transparent material is important for optical application. In order to provide a glass suitable for laser processing, JP11(1999)-217237A discloses a technique for providing glass in which cracks tend not to occur by decreasing the laser processing threshold value through the introduction of silver into glass by ion exchange.

[0006]

[Problem to be solved by the invention]

Glass containing a large amount of alkali metal allows silver ions to be introduced thereinto by a silver ion exchange. However, a phenomenon occurs in which silver ions are reduced in the vicinity of the glass surface and thereby are inhibited from diffusing into the glass. Hence, the effective laser processing region is limited to the vicinity of the glass surface and therefore it still is

difficult to carry out processing of glass including processing of the inner part thereof, for instance, processing to make a through hole in a glass sheet. In addition, there is another problem that the ion exchange rate is low and it therefore is difficult to allow ions to reach the inner part of glass stably.

[0007]

Moreover, glass for laser processing produced through the silver ion exchange contains a large amount of alkali metal or alkaline-earth metal and therefore has a high thermal expansion coefficient, which is a problem. Since heat is generated in a laser irradiation part during laser processing, the laser irradiation part and the vicinity thereof are deformed due to the stress caused by the difference in thermal expansion between them. When the thermal expansion coefficient is high, the size of a processing part measured during laser irradiation varies from that measured after laser irradiation. Hence, the dimensional accuracy of the processing part may deteriorate.

[0008]

Furthermore, with respect to optical elements, it generally is desirable that the dimensional change that is caused by a temperature change be small. There also is a problem that such a dimensional change as described above may cause variations in the characteristics of optical elements.

In order to solve the above-mentioned problems, the present invention is intended to provide a glass for laser processing that can be laser-processed to the inner part thereof, such as for making a through hole in the glass, and has a lower thermal expansion coefficient compared with a conventional glass.

[0009]

[Means for solving problem]

A glass for laser processing according to the present invention that can be laser-processed by causing ablation or evaporation by laser beam energy absorbed therein contains titanium in the form of an atom, colloid or ion and has a composition that satisfies the following conditions:

$$60 \leq \text{SiO}_2 + \text{B}_2\text{O}_3 \leq 79 \text{ mol\%};$$

$$5 \leq \text{Al}_2\text{O}_3 + \text{TiO}_2 \leq 20 \text{ mol\%}; \text{ and}$$

$$5 \leq \text{LiO}_2 + \text{Na}_2\text{O} + \text{K}_2\text{O} + \text{Rb}_2\text{O} + \text{Cs}_2\text{O} + \text{MgO} + \text{CaO} + \text{SrO} + \text{BaO} \leq 20 \text{ mol\%},$$

wherein  $5 \leq \text{TiO}_2 \leq 20 \text{ mol\%}$ .

[0010]

In the glass having the composition described above,  $\text{SiO}_2$  or  $\text{B}_2\text{O}_3$  is an oxide that forms a

network of the glass, and it forms a skeleton of the glass. Furthermore, since Li<sub>2</sub>O, Na<sub>2</sub>O, K<sub>2</sub>O, Rb<sub>2</sub>O, Cs<sub>2</sub>O, MgO, CaO, SrO, or BaO, which is a modifier oxide, breaks part of the network structure of the glass, it is used for reducing viscosity to be obtained at high temperatures or decreasing the temperature gradient of viscosity.

[0011]

Al<sub>2</sub>O<sub>3</sub> or TiO<sub>2</sub> is an intermediate oxide and can be present in the glass as either a network forming oxide or a modifier oxide according to the balance between SiO<sub>2</sub> or B<sub>2</sub>O<sub>3</sub>, which is a network forming oxide, and Li<sub>2</sub>O, Na<sub>2</sub>O, K<sub>2</sub>O, Rb<sub>2</sub>O, Cs<sub>2</sub>O, MgO, CaO, SrO, or BaO, which is a modifier oxide. Particularly, TiO<sub>2</sub> is necessary for lowering the laser processing threshold value.

[0012]

The glass having the composition described above is allowed to have a low thermal expansion coefficient by increasing the content of the component SiO<sub>2</sub> or B<sub>2</sub>O<sub>3</sub>, which is a network forming oxide, and minimizing the content of Li<sub>2</sub>O, Na<sub>2</sub>O, K<sub>2</sub>O, Rb<sub>2</sub>O, Cs<sub>2</sub>O, MgO, CaO, SrO, or BaO, which is a modifier oxide.

[0013]

In order to obtain more uniform glass with a common melting method, it is desirable that the composition satisfy the following condition, within the composition range described above:

$$(Al_2O_3 + TiO_2) / (Li_2O + Na_2O + K_2O + Rb_2O + Cs_2O + MgO + CaO + SrO + BaO) \leq 0.9.$$

[0014]

Moreover, from the viewpoint of both the decrease in thermal expansion coefficient and improvement in laser processability, a most preferable composition satisfies the following ranges:

$$70 \leq SiO_2 + B_2O_3 \leq 79 \text{ mol\%};$$

$$10 \leq TiO_2 \leq 15 \text{ mol\%}; \text{ and}$$

$$10 \leq Na_2O \leq 15 \text{ mol\%}.$$

[0015]

When glass absorbs laser beams, variations in glass structure or absorptance occur to cause ablation or evaporation. The glass having the aforementioned composition of the present invention requires less energy to be processed by causing the phenomenon and therefore has a low processing threshold value. Furthermore, the glass for laser processing of the present invention is not modified through, for instance, an ion exchange but is allowed to have a necessary composition by melting. Accordingly, the composition of the glass is substantially uniform in the thickness direction. Hence, it is possible to carry out easily not only processing of the vicinity of the glass

surface but also processing of the inner part of the glass, such as, for instance, processing for making a through hole in a glass sheet.

[0016]

[Mode for carrying out the invention]

The present invention is intended to improve the laser processability of glass and further to allow the glass to be processed at low energy from a surface toward an inner part of the glass. Hence, uniform glass has to be produced. Whether or not uniform glass is made was examined by actual melting, casting and slow cooling.

[0017]

Raw materials were blended so that 200 g of glass was to be produced. This was put into a platinum crucible, which then was placed in a melting furnace whose temperature had been raised to about 1500°C. This was maintained for six hours while being stirred midway through the process. Casting was carried out by pouring the glass on an iron plate. Immediately thereafter, it was placed in an annealing furnace whose temperature had been raised to about 500°C. It then was maintained at a predetermined temperature for 30 minutes and then was cooled slowly to room temperature over 16 hours. A glass block thus obtained was cut and polished by a common method. Thus a sheet-like sample of glass for laser processing with smooth surfaces was prepared.

[0018]

The laser processing threshold value was measured using an optical system 1 shown in FIG. 1. Ultraviolet rays with wavelengths of 266 nm and 355 nm of the Nd:YAG laser were used as the laser beam 10. This laser had a pulse rate of 20 Hz and a pulse width of 5 to 8 nm. The laser beam 10 was focused by a lens (not shown in FIG. 1) whose focal length was 100 mm. The glass sample 20 attached to the sample holder 22 located on the sample stage 24 was irradiated with the laser beam 10 thus focused. The irradiation time was controlled with an irradiation shutter 30 and was set at two seconds.

[0019]

Energy of the laser beam 10 was measured with a power meter 40 placed on an optical path of the laser beam 10 in the state where the irradiation shutter 30 was closed. The sample was irradiated with laser beams whose energy level was changed variously by the attenuator 50, and the amount of energy used at the limit of causing ablation was determined, which was defined as the processing threshold value.

[0020]

The laser source 12 generates high energy beams. Hence, for ensuring safety, the laser source 12 can be controlled remotely. A device 14 that supplies power and cooling water to the laser source 12 is operated with a remote controller 16. The laser source 12 itself also contains a shutter although it is not specifically shown in FIG. 1. This shutter also can be controlled remotely. Laser beams that have passed through the glass sample 20 are absorbed by a beam damper 18.

Examples in which the present invention is used are described below, but the present invention is not limited to them.

#### [0021]

##### [Examples]

The compositions of glasses for laser processing of the present invention according to Examples 1 to 12 are indicated in Table 1. The compositions of respective components are within the following ranges:

- network forming oxides ( $\text{SiO}_2$  and  $\text{B}_2\text{O}_3$ ): 60.0 to 79.0 mol%;
- intermediate oxides ( $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$ ): 5.0 to 20.0 mol%,  
wherein the content of  $\text{TiO}_2$  must be 5.0 to 20.0 mol%; and
- modifier oxides ( $\text{Li}_2\text{O}$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{SrO}$ , and  $\text{BaO}$ ): 5.0 to 20.0 mol%.

The glass for laser processing of the present invention consists substantially only of the compositions described above except for a very small amount of impurities.

#### [0022]

The samples of glasses for laser processing melted in the compositions mentioned above were irradiated with respective laser beams having wavelengths of 266 nm and 355 nm, with the irradiation energy being varied. Table 1 shows the processing threshold values obtained as a result.

It can be understood that in both the cases of using the respective wavelengths, the processing threshold value decreases considerably with an increase in concentration of  $\text{TiO}_2$ . However, the processing threshold value hardly depends on the compositions of the network forming oxides and modifier oxides.

#### [0023]

FIG. 2 shows vitrification conditions of respective compositions, with the relationship between the total amount of  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$  and the amount of  $\text{Na}_2\text{O}$  being plotted with respect to various compositions tested by the inventors. It can be understood from FIG. 2 that an excessively small amount of modifier oxides that are typified by  $\text{Na}_2\text{O}$  causes phase splitting and devitrification

and thus prevents uniform glass from being produced. That is, as shown in FIG. 2, in order to produce uniform glass, a relationship of

$$(Al_2O_3 + TiO_2) / (Li_2O + Na_2O + K_2O + Rb_2O + Cs_2O + MgO + CaO + SrO + BaO) \leq 0.9 \quad (1)$$

must hold.

As described above, in order to decrease the laser processing threshold value, the glass needs to contain a large amount of  $TiO_2$ . In this case, in order to satisfy the condition of the formula (1), it is necessary to increase the concentration of the modifier oxides. The increase in concentration of the modifier oxides, however, generally results in an increase in thermal expansion coefficient. Accordingly, it can be understood that the decrease in the processing threshold value and the decrease in the thermal expansion coefficient have a trade-off relationship.

#### [0024]

##### [Comparative Example]

Comparative Example 1 is a so-called soda-lime glass that is used for common window glass, for instance. The processing threshold values were determined in the same manner as in the examples. The maximum power was 1.10 W at a laser beam wavelength of 266 nm while it was 2.10 W at a laser beam wavelength of 355 nm. In both the cases, neither ablation nor evaporation occurred and thus no change was observed in the sample. Compositions having a very low concentration of  $TiO_2$  or  $Al_2O_3$ , which is an intermediate oxide, or containing no  $TiO_2$  or  $Al_2O_3$ , result in extremely high processing threshold values.

#### [0025]

As shown in Table 1, Comparative Example 2 is a material containing  $TiO_2$ , which is an intermediate oxide, and  $Na_2O$ , which is a modifier oxide, each of which has a high concentration exceeding 20 mol%. The processing threshold values were determined in the same manner as in the examples and were very low, specifically 15 mW and 200 mW at laser beam wavelengths of 266 nm and 355 nm, respectively. However, the glasses having compositions of the examples have thermal expansion coefficients that are lower than  $100 \times 10^{-7} \text{ }^{\circ}\text{C}^{-1}$  while the glass having the composition of this comparative example has a thermal expansion coefficient as high as  $118 \times 10^{-7} \text{ }^{\circ}\text{C}^{-1}$ .

#### [0026]

When the examples and comparative examples described above are taken into account, it turns out that in obtaining a glass whose thermal expansion coefficient is as low as possible and whose processing threshold value also is low, the most preferable compositions are compositions

that are typified by Examples 11 and 12, i.e. compositions that satisfy the condition of the formula

(1) described above and additionally are in the following ranges:

$$70 \leq \text{SiO}_2 + \text{B}_2\text{O}_3 \leq 79 \text{ mol\%};$$

$$10 \leq \text{TiO}_2 \leq 15 \text{ mol\%}; \text{ and}$$

$$10 \leq \text{Na}_2\text{O} \leq 15 \text{ mol\%}.$$

[0027]

[Table 1]

Components (mol%)	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7
SiO <sub>2</sub>	60	60	60	60	60	60	60
B <sub>2</sub> O <sub>3</sub>	0	0	0	0	0	0	0
TiO <sub>2</sub>	10	20	20	20	20	10	20
Al <sub>2</sub> O <sub>3</sub>	10	0	0	0	0	10	0
Na <sub>2</sub> O	10	20	15	15	15	15	15
Li <sub>2</sub> O	0	0	5	0	0	0	0
K <sub>2</sub> O	0	0	0	5	0	0	0
MgO	0	0	0	0	5	0	0
CaO	0	0	0	0	0	0	5
SrO	0	0	0	0	0	0	0
BaO	10	0	0	0	0	100	100
Total	100	100	100	100	100	100	100
Processing threshold val. (mW)						25	25
Wavelength : 266nm	60	25	25	25	25	300	300
Wavelength : 355nm	500	300	300	300	300	89	90
Thermal expansion coef. (°C <sup>-1</sup> )	82	97	94	99	86	100	100

Components (mol%)	Example 8	Example 9	Example 10	Example 11	Example 12	C. Ex. 1	C. Ex. 2
SiO <sub>2</sub>	60	60	60	60	65	72	37.5
B <sub>2</sub> O <sub>3</sub>	0	0	10	10	10	0	12.5
TiO <sub>2</sub>	20	20	10	15	12.5	0	25
Al <sub>2</sub> O <sub>3</sub>	0	0	0	0	0	0.9	0
Na <sub>2</sub> O	15	10	10	15	12.5	12.7	25
Li <sub>2</sub> O	0	0	0	0	0	0	0
K <sub>2</sub> O	0	0	0	0	0	6	0
MgO	0	0	0	0	0	8.4	0
CaO	0	0	0	0	0	0	0
SrO	0	0	0	0	0	0	0
BaO	5	10	10	0	100	100	100
Total	100	100	100	100	100	100	100
Processing threshold val. (mW)						-	15
Wavelength: 266nm	25	25	60	30	30	-	200
Wavelength: 355nm	300	300	500	400	400	-	118
Thermal expansion coef. (°C <sup>-1</sup> )	91	87	82	75	64	-	89

[0028]

[Effects of the invention]

The present invention can provide a glass for laser processing that has a low laser processing threshold value as well as a low thermal expansion coefficient. In other words, the glass for laser processing of the present invention requires less laser beam energy to be processed and is affected less by heat. Thus, the glass for laser processing can be processed more precisely.

[BRIEF DESCRIPTION OF THE DRAWINGS]

[FIG. 1] FIG. 1 is a schematic view showing an optical system used for measuring a laser processing threshold value.

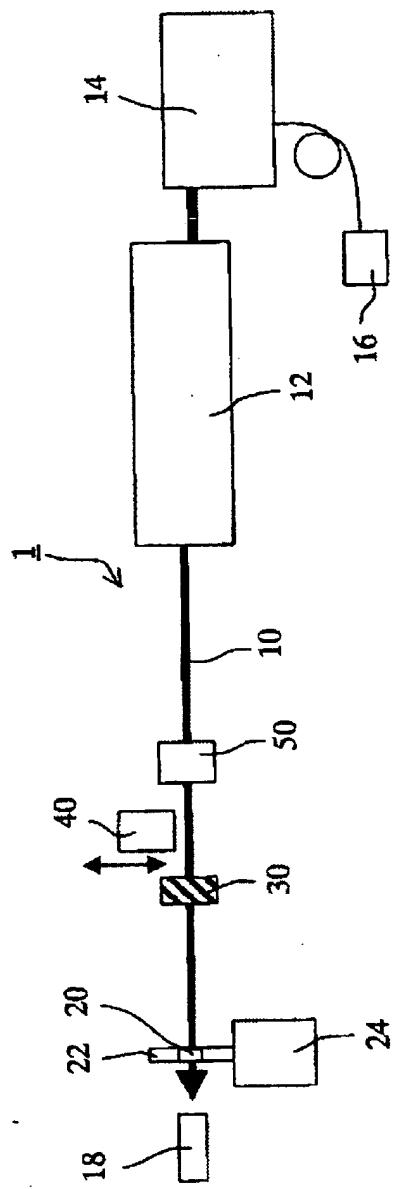
[FIG. 2] FIG. 2 is a diagram showing a composition range in which uniform glass can be produced.

[Explanation of letters or numerals]

- 10 Laser Beam
- 12 Laser Source
- 20 Glass Sample
- 22 Sample Holder
- 24 Sample Stage
- 30 Irradiation Shutter
- 40 Power Meter
- 50 Attenuator

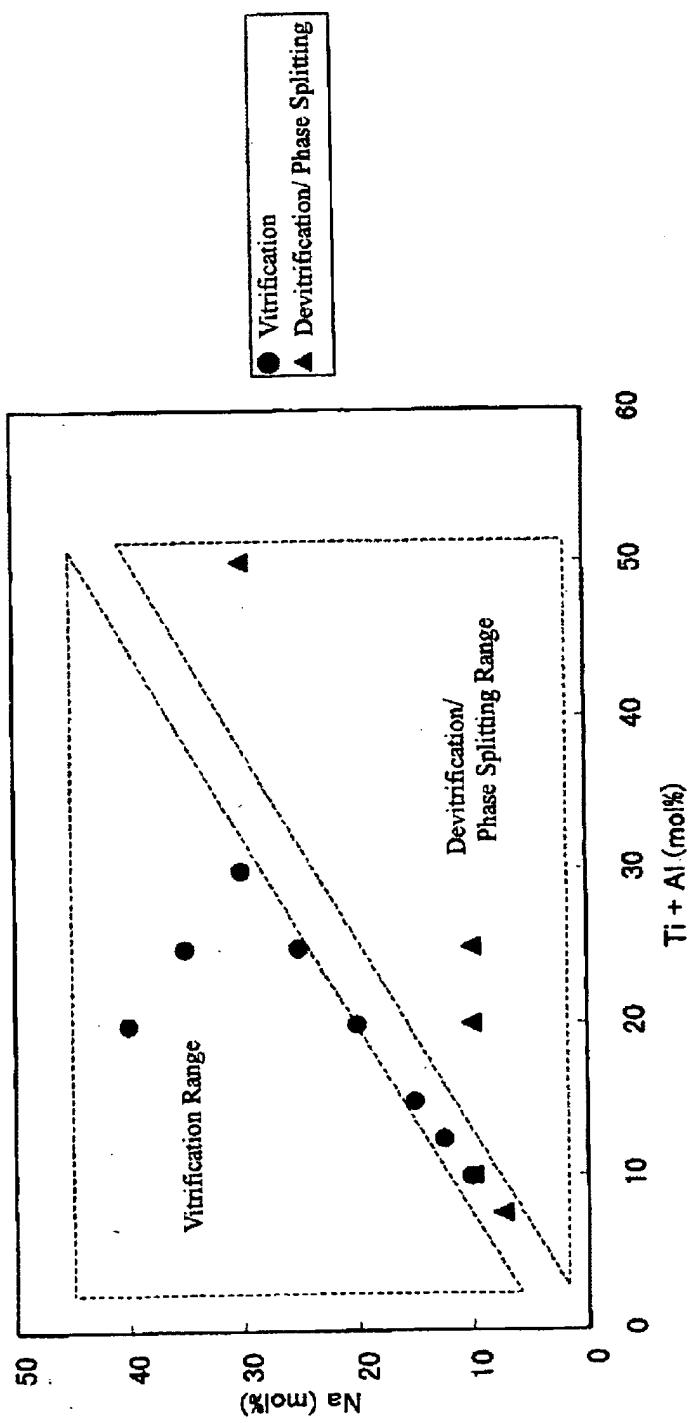
2002-214983

[Document Name] Drawings  
[FIG. 1]



2002-214983

[FIG. 2]



[Document Name] ABSTRACT

[Abstract]

[Object] A glass for laser processing that can be laser-processed to the inner part thereof, such as for making a through hole in the glass, by causing ablation or evaporation by laser beam energy absorbed therein, has a low thermal expansion coefficient and can be processed precisely is provided.

[Means to Solve the Problems] A glass for laser processing according to the present invention contains titanium in the form of an atom, colloid or ion and has a composition that are within the following ranges. That is, the total amount of network forming oxides ( $\text{SiO}_2$ ,  $\text{B}_2\text{O}_3$ ) ranges from 60 to 79 mol%, the total amount of intermediate oxides ( $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ) ranges from 5 to 20 mol%, and the total amount of modifier oxides ( $\text{Li}_2\text{O}$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{Rb}_2\text{O}$ ,  $\text{Cs}_2\text{O}$ ,  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{SrO}$ ,  $\text{BaO}$ ) ranges from 5 to 20 mol%, wherein the content of  $\text{TiO}_2$  must be 5 to 20 mol%. Also, it is desired that the total amount of the intermediate oxides should be not greater than 90% of the total amount of the modifier oxides.

[Selected Figure] FIG. 2